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Measurement of contemporary and fossil carbon contents of PM_{2.5} aerosols:
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Abstract

The impact of aerosol particulate matter of mean mass aerodynamic diameter $\leq 2.5 \mu\text{m}$ (PM_{2.5} aerosols), on health, visibility, and compliance with EPA's regional haze regulations is a growing concern. Techniques that can help better characterize particulate matter are required to better understand the constituents, causes and sources of PM_{2.5} aerosols. Measurement of the $^{14}\text{C}/\text{C}$ ratio of the PM_{2.5} aerosols, the absence of ^{14}C in fossil carbon materials and the known $^{14}\text{C}/\text{C}$ levels in contemporary carbon materials allows use of a two-component model to derive contemporary and fossil carbon contents of the particulate matter. Such data can be used to estimate the relative contributions of fossil fuels and biogenic aerosols to the total aerosol loading. Here, the methodology for performing such an assessment using total suspended particulate Hi-vol aerosol samplers to collect PM_{2.5} aerosols on quartz fiber filters and the technique of accelerator mass spectrometry to measure $^{14}\text{C}/\text{C}$ ratios is presented and illustrated using PM_{2.5} aerosols collected at Yosemite National Park.

Introduction

On July 18, 1997, the Environmental Protection Agency (EPA) issued revised National Ambient Air Quality Standards (NAAQS) particulate matter (PM) [1]. In actions for PM_{2.5} aerosols (particles with mean mass aerodynamic diameter $\leq 2.5 \mu\text{m}$) NAAQS, EPA has determined that visibility impairment due to regional haze is a PM_{2.5} effect of concern [2]. Consequently, the impact of PM_{2.5} aerosols, on health, visibility, and compliance with EPA's regional haze regulations is a growing concern. Techniques that can help better characterize particulate matter are required to better understand the causes and sources of PM_{2.5} aerosols.

Radiocarbon (^{14}C) is a naturally occurring radioisotope, produced in the atmosphere by cosmic ray interaction with ^{14}N . It oxidizes to CO_2 , and enters the food chain through plant photosynthesis, so that all living things are intrinsically labeled with a characteristic $^{14}\text{C}/\text{C}$ ratio. Atmospheric nuclear testing produced large additional quantities of ^{14}C in the late 50's and early 60's: the radiocarbon content of the atmosphere doubled in the northern hemisphere between 1955 and 1963 [3]. Since the almost complete cessation of atmospheric testing in 1964, atmospheric ^{14}C levels have been declining as this excess is mixed into the biosphere. The present atmospheric $^{14}\text{C}/\text{C}$ ratio, expressed in terms of the "Modern" radiocarbon nomenclature [4], is 109 percent Modern Carbon (pMC) [5], or 1.09 times Modern (fraction modern). The carbon content of materials that possess $^{14}\text{C}/\text{C}$ ratios that are similar to the present atmospheric $^{14}\text{C}/\text{C}$ level is often described as contemporary carbon and such materials are often referred to as containing contemporary radiocarbon levels.

Carbon that constitutes contemporary aerosol particulate matter is primarily biogenic in origin arising from the growth, natural biologic processes, destruction and anthropogenic use of

trees and plants. Trees and other perennial plants contain a year-by-year record of atmospheric ^{14}C in the radiocarbon content of their wood, leaves, etc. Leaves and small twigs have $^{14}\text{C}/\text{C}$ ratios at or close to the present 1.09 fraction modern. The interiors of larger branches - wood from close to the time of atmospheric testing - contain more ^{14}C . Inner rings of old trees dating from before atmospheric nuclear testing have ^{14}C levels below Modern.

Thus, carbon containing aerosols derived from trees and plants, unless they come from greater than 45 -year old wood, will tend to contain radiocarbon levels at or above Modern. However, the exact levels will depend on the source material and may even vary with time in the case of sources such as wood smoke arising from fire burning into large branches or logs spanning significant numbers of years of different ^{14}C concentration.

In contrast, fossil fuel -derived materials are made from carbon that was sequestered underground for periods that were very long compared to the 5730 -year half -life of ^{14}C . Hence oil, coal and materials and particles derived from these feed stocks, are radiocarbon -free. The carbon content of materials that possess no ^{14}C is often described as fossil carbon and such materials are often referred to as fossil carbon material.

Other sources of carbon in the particulate matter can arise from carbonate dust and soil organics. Carbonates will provide an additional source of material that frequently contains no ^{14}C and can thus have a $^{14}\text{C}/\text{C}$ ratio that is identical to that of fossil carbon material, while radiocarbon activities of soil organics are typically close to, or slightly lower than, those of contemporary carbon materials [6].

In principle, the absence of ^{14}C in fossil carbon materials and the known $^{14}\text{C}/\text{C}$ levels in contemporary carbon materials provides a method to determine contemporary and fossil carbon contents of PM_{2.5} aerosols if the $^{14}\text{C}/\text{C}$ ratio of the PM_{2.5} aerosols can be measured and if contributions from soil organics and carbonates are small. Here, the methodology for performing

such an assessment using aerosol samplers to collect PM_{2.5} aerosols on quartz fiber filters and the technique of accelerator mass spectrometry (AMS) to measure $^{14}\text{C}/\text{C}$ ratios is presented and illustrated using PM_{2.5} aerosols collected on quartz fiber filters at during the summer of 2002 at Turtleback dome, Yosemite National Park.

ExperimentalSection

SampleCollection

Aerosol particulate matter was sampled at Turtleback Dome, Yosemite National Park at an elevation of 1605 meters above sea level. Samples were collected using a Thermo Anderson TotalSuspendedParticulate(TSP)Hi -VolsamplerwithaSA -230-Fimpactorplate. Thesampler wasoperatedatavolumetricflowof 1130l/minute toyieldaPM2.5sampleonthebackup. One slotted glass fiber substrate was installed in the Hi -Vol impactor head per sampling period to collectparticlesgreaterthan2 .5microns. Theglassfibersubstrateswerestoredinsealedplastic bagspriortouse, wereonlyusedforsizingandwerediscardedfollowingsampling. One(20x 25cm²)quartzfiberfilter(GellmanQM -A)persamplingperiodwasusedasthebackupfilterto collectPM2.5 aerosols. Thequartzfilterswerepre -firedbybakingat600 °Cfor12hoursand storedinsealedplasticbagspriortouse.

PM 2.5 aerosols were sampled daily from approximately 8:00 am to 8:00 pm Pacific standardtimefromJuly14th roughSeptember3,2002. Overthecourseofthecollectionperiods theprevailingwinddirectionwasfromthewest -southwestcorrespondingtoupslopeflowfrom theSanJoaquinvalleybelowYosemiteNationalpark .Inmanyinstances12 -hoursamplingwas utilized on the same quartz filter for 3 consecutive days for a total sampling of 36 hours. However, when anticipated climate conditions suggested PM 2.5 levels might be substantially higherthanaverage,quartzfilterswerechangeddailyoronceeverytwo days.

Thirteenquartzfilters,includingthreeatbeginning,threetowards themiddleandtwoat theendofthestudyactedasvehiclecontrols. Eachofthesefilterswasplacedinthesamplerfor tenminuteswhenitwasnotoperating.

Following deployment quartz filters were immediately placed in new resealable plastic bags. The bagged filters were stored flat and unfolded in a cool dry, dark environment within a plastic container prior to shipment to Lawrence Livermore National Laboratory (LLNL) for analysis.

Sample preparation

At LLNL areal samples of size 25 cm^2 ($5 \times 5\text{ cm}$) were cut with a knife from the central region of each quartz filter. Each sample was directly combusted in vacuum at 900°C with CuO oxidizer in a sealed quartz tube. CO_2 from the combustion was cryogenically isolated from other combustion products and measured manometrically before conversion to graphite by hydrogen reduction using a cobalt catalyst [7,8].

$^{14}\text{C}/\text{C}$ ratios for the graphite samples were measured by AMS at LLNL [9]. The data were reported as a fraction of the Modern radiocarbon standard (fraction Modern or FM) [4]. Measurements of CO_2 obtained from combustion of duplicate areal samples by conventional mass spectrometry produced $\delta^{13}\text{C}$ values varying between -22 and -27 permil averaging -25 ± 1 permil. The average $\delta^{13}\text{C}$ value was assumed for all PM_{2.5} aerosol samples in order to correct the radiocarbon measurements for isotopic fractionation effects.

Duplicate radiocarbon analyses were performed on eight randomly selected PM_{2.5} aerosol laden filters. For the replicate analysis, another square 25 cm^2 region towards the edge of the filter was analyzed.

Data reduction and analysis

The geologic and atmospheric factors present during the sampling period suggested that it was justifiable to consider the carbon content of the PM_{2.5} aerosols as a two-component

mixture of contemporary and fossil carbon (see Results and Discussion). For an aerosol particulate matter whose carbon content is dominated by contemporary and/or fossil carbon, measurement of the $^{14}\text{C}/\text{C}$ ratio and knowledge of the $^{14}\text{C}/\text{C}$ levels in contemporary carbon affords use of a simple two-component method to determine the contemporary and fossil carbon contents. If R_a is the $^{14}\text{C}/\text{C}$ ratio of the PM 2.5 aerosol sample and R_c is the $^{14}\text{C}/\text{C}$ ratio of the contemporary component, then the fraction F_c of the carbon on the filter that is derived from contemporary carbon is given by:

$$F_c = R_a / R_c \quad (1)$$

because all of the radiocarbon must come from the contemporary fraction. Over the period from 1997 to 2002 the fraction Modern of contemporary samples slowly decreased from 1.11 to 1.09 [5, 10]. Hence, for this study, R_c (the $^{14}\text{C}/\text{C}$ ratio of the contemporary component) was assumed to be 1.10 ± 0.02 .

To account for any endogenous carbon on the quartz filters prior to sampling PM 2.5 aerosols measured $^{14}\text{C}/\text{C}$ ratios were corrected using the mixing equation:

$$R_a = R_m * L_m / (L_m - L_b) - R_b * L_b / (L_m - L_b) \quad (2)$$

where R_a is the $^{14}\text{C}/\text{C}$ ratio of the PM 2.5 aerosol, R_m is the measured $^{14}\text{C}/\text{C}$ ratio of the PM 2.5 aerosol laden filter, L_m is the carbon mass of the analyzed region of the filter, L_b is the carbon mass on the analyzed region of a blank filter, R_b is the $^{14}\text{C}/\text{C}$ ratio of a blank filter, and $L_m - L_b$

is the blank -corrected PM_{2.5} aerosol carbon mass. Uncertainties in R_a were derived from those in the measured quantities using standard error propagation relationships.

Contemporary and fossil carbon masses (μg) in the PM_{2.5} aerosol were derived using equation (1) with R_a determined by equation (2). Total, contemporary and fossil carbon masses were converted to PM_{2.5} aerosol concentrations (units of $\mu\text{g}/\text{m}^3$) using the volume of air sampled for each sampling period, the area of the quartz filter analyzed via AMS and the total area of the quartz fiber filter through which the sampled air was drawn.

Results and Discussion

The average (mean \pm standard deviation) values of carbon mass and fraction Modern obtained from the thirteen blank filters were 0.053 ± 0.013 mg and 0.7919 ± 0.1030 Fraction Modern (FM) respectively. These values were used to correct analyses of PM_{2.5} aerosol laden filter samples for contributions from endogenous filter carbon.

Replicate analyses of the eight randomly selected PM_{2.5} aerosol laden filters revealed consistency in both mass of carbon and associated fraction Modern to within measurement uncertainties corresponding to one sigma values of 0.02 mg for mass and 0.005 for FM for each filter. This suggests that the sampled area of 5x 5 cm yields carbon loadings and fraction Modern that are representative of the whole filter.

Table 1 shows the total carbon content and associated fraction Modern of the PM_{2.5} aerosol from the sampled area of each laden filter. Contemporary and fossil carbon contents of the aerosols derived from the data in Table 1 using the two component model described in equation 1 are plotted against total carbon content in Figure 1.

Use of the two -component model to derive fossil and contemporary carbon contents assumes that contributions from non -fossil and non -contemporary sources of carbon during the sampling periods were non -existent or small. It may not be valid to use the model if other sources of carbon contribute significantly to the aerosol particulate matter, as multi -component mixtures must then be considered. The presence of significant quantities of carbonates in particulate matter can lead the model to overestimate the fossil carbon content while the presence of soil organics can lead the model to overestimate the contemporary carbon content.

For the summer of 2002 at Turtleback Dome there is a wealth of data that justifies application of the two -component model to the data in Table 1. First of all, Turtleback dome is

composed of granite and the sampler was installed on bedrock at the summit with little soil present in the vicinity of the sampler. In addition, visibility at the sampling site was periodically impaired due to significant contributions from smoke derived from wildfires for several periods in the study [11, 12]. PM_{2.5} aerosol organic carbon contents at Turtleback dome during the summer of 2002 are consistent with significant smoke contributions periodically impairing visibility. PM_{2.5} aerosol organic carbon contents were substantially higher than the historical average of $\sim 3 \mu\text{g}/\text{m}^3$ and varied between 2 and $10 \mu\text{g}/\text{m}^3$, averaging $\sim 5.5 \mu\text{g}/\text{m}^3$, while total carbon contents averaged $\sim 6 \mu\text{g}/\text{m}^3$ [11, 12]. These geologic, and atmospheric factors suggest that contributions from non-fossil and non-contemporary sources of carbon during the sampling periods were minimal and that it is justifiable to consider the carbon contents of the PM_{2.5} aerosols as a two-component mixture of contemporary and fossil carbon.

The data in Figure 1 reveal that the fossil carbon concentration appears to be constant at $\sim 0.7 \pm 0.1 \mu\text{g}/\text{m}^3$ and is independent of the total carbon content of the PM_{2.5} aerosol. Conversely, the contemporary carbon content varies in direct proportion to the total carbon content of the PM_{2.5} aerosols with a gradient of 0.9997, an intercept of -0.7 and a coefficient of correlation of 0.99. This implies that variation in the total carbon loading at Turtleback Dome arises solely from variation in the contemporary carbon loading of the PM_{2.5} aerosols.

Several inferences can be drawn from the two-component modeling. Because the aerosol PM_{2.5} fossil carbon content was effectively constant during the study period and typically much smaller than the contemporary carbon content, it is unlikely that fossil fuel emissions contributed significantly to periods of impaired visibility at Yosemite during the summer of 2002. In addition, since carbon that constitutes contemporary aerosol particulate matter is primarily biogenic in origin, the data in Figure 1 suggest that the majority of PM_{2.5} aerosol carbon at

Yosemite during the summer of 2002 was biogenic in origin. The large variability in PM_{2.5} aerosol contemporary carbon contents observed in Figure 1 likely arises from significant variations in a biogenic source or sources. It is not the purpose of this paper to make a detailed investigation of the cause of this variability. However, as visibility at the sampling site was periodically impaired due to significant contributions from smoke for several periods in the study [11,12], a plausible biogenic source for at least some of the variability is smoke from wildfires.

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Tables

Table 1: Carbon content and the associated fraction modern (FM) of PM_{2.5} aerosols obtained from the sampled area of each aerosol filter.

Sample¹	Corrected C mass (mg)²	+/-	Corrected FM²	+/-
7/14-16/02	0.557	0.023	0.8460	0.0524
7/17-19/02	0.507	0.023	0.8139	0.0558
7/20-21/02	0.437	0.023	0.8008	0.0639
7/22-24/02	0.627	0.023	0.8838	0.0481
7/25-27/02	0.627	0.023	0.8821	0.0480
7/28/02	0.357	0.023	0.8965	0.0850
7/29/02	0.297	0.023	0.9483	0.1066
7/30/02	0.317	0.023	0.9725	0.1019
7/31-8/2/02	0.657	0.023	0.9513	0.0487
8/3-8/5/02	0.787	0.023	0.9465	0.0406
8/6-7/02	0.357	0.023	0.9265	0.0873
8/8-9/02	0.527	0.023	0.9596	0.0614
8/10/02	0.347	0.023	0.9665	0.0928
8/11-13/02	0.867	0.023	0.9736	0.0378
8/14/02	0.457	0.023	1.0316	0.0747
8/15/02	0.477	0.023	1.0471	0.0726
8/16-18/02	0.907	0.023	1.0473	0.0388
8/19-21/02	0.907	0.023	1.0315	0.0382
8/22-24/02	0.687	0.023	0.9410	0.0463
8/25-27/02	0.797	0.023	0.9751	0.0410
8/28-30/02	0.717	0.023	0.9351	0.0440
8/31-9/1/02	0.327	0.023	0.9348	0.0958
9/2-3/02	0.227	0.023	0.9361	0.1377

¹Sample description refers to the date or dates of sampling for a filter.

² Carbon masses and fraction Moderns have been corrected using equation 2 for contributions from endogenous carbon on blank filters.

Figure Captions

Figure 1: Graph of contemporary carbon (black squares) and fossil carbon (crosses) concentration versus total carbon concentration for PM 2.5 aerosols collected at Turtleback dome from July 14 through September 3 2002. The solid lines are linear least squares fits to the data. The least squares fit to the contemporary carbon data has a gradient of 0.9997 and a coefficient of correlation of 0.99. The least squares fit to the fossil carbon data has a gradient of -0.00007.

Figures.

Figure1:

